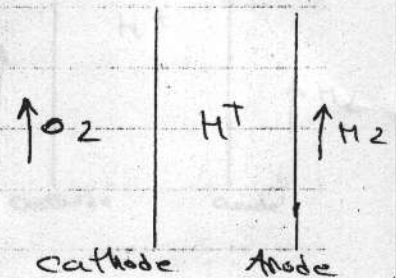lecture 3   د. عمر الفاروق

* <u>Electrolytes of different fuel cells</u>:-

① <u>SPE (up to 800°C)</u>

* <u>Cathode rxn</u>

$$\frac{1}{2}O_2 + 2H^+ + 2e^1 \rightarrow H_2O$$

* <u>Anode rxn</u>

$$H_2 \rightarrow 2H^+ + 2e^1$$
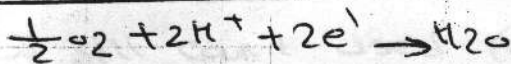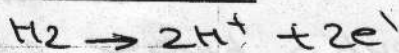
② <u>AFC</u>

* operates in the range of (100-120°C)

* <u>Cathode reaction</u>

$$\frac{1}{2}O_2 + H_2O + 2e^1 \rightarrow 2OH^-$$

* <u>Anode reaction</u>

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^1$$

* <u>overall rx</u>

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$
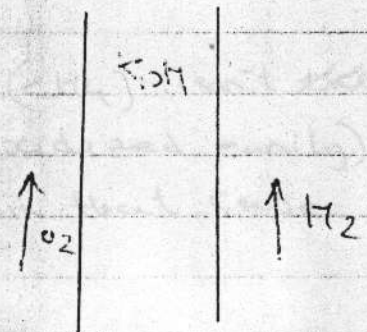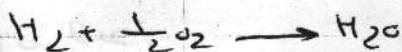
<u>Note</u>
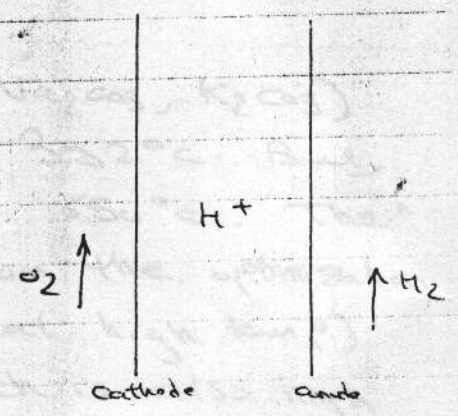
_ The previous 2 types can only be used for mobile sources because of :-

1) their high cost

2) subjected to poisoning by (Co); so overpotential is high ⟹ and the resulting potential is very low.   as they're operating at low temp.

- OH⁻ ions carry the charges as well as the electrons

- The liq. electrolyte is held in a matrix unlike the solid electrolyte in SPE.

③ pAFc

* operates till 200°C
* The same cathode and anode reactions as above.
* This electrolyte isn't very sensitive to low concentration of (CO), but we still can't used (CO) as a fuel.
* In addition to the above advantage, the second advantage for (pAFc) is that we can use (Hc) as a fuel, as CO_2 doesn't cause problems in this case

Note

N.G can be used as fuel ⇒ but (CH_4) isn't ~~electrode~~ electrochemically active (i.e ; isn't oxidized easily), so certain catalysts must be used in that case.

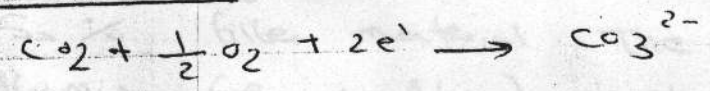$$O_2 \uparrow \qquad H^+ \qquad \uparrow H_2$$

Cathode   anode

④ MCFc

- for low temp. fuel cells, H_2 can be used as a fuel.
- for high temp. fuel cells, H_2 or (CO) can be used as a fuel

$$\uparrow O_2 + CO_2 \qquad \uparrow fuel$$

Cathode rxn

$$CO_2 + \frac{1}{2} O_2 + 2e^1 \longrightarrow CO_3^{2-}$$

Anode rxn

$$CO + CO_3^{2-} \longrightarrow 2CO_2 + 2e^1$$

overall rxn

$$CO + \frac{1}{2} O_2 \longrightarrow CO_2$$

$$\longrightarrow$$
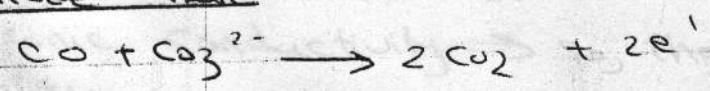
Notes

* for the famous system (Li_2CO_3, Na_2CO_3, K_2CO_3) form eutectic mix. at about $352°C$. But, we operate this system at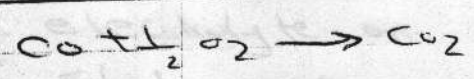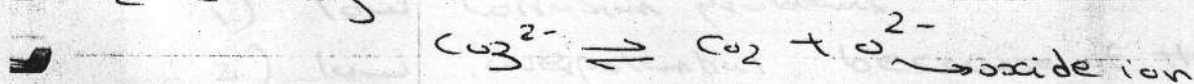 about $650°C$. The previous temp comes from the optimization between the high rate of rxn. (at high temp) and the corrosive action (which is also high at high temp.)

* Molten carbonates cause severe corrosion.

* The CO_2 formed is recycled to the cathode

* The CO_2 is entered with O_2 in the cathode so as to prevent the formation of oxide ion if O_2 is only used.

$$CO_3^{2-} \rightleftharpoons CO_2 + O^{2-} \text{ oxide ion}$$

The previous rxn. shows that if (CO_2) isn't found, oxide ion will be formed by dissociation of (CO_3^{2-}).

- The formed oxide ion will cause the formation of metal oxide which is a barrier against the passage of current.

* The optimum % of CO_2 and O_2 is $2 : 1$

* we can use other mixtures of solids with lower eutectic temp., but we prefer carbonates in case of use of (CO) as a fuel.

* The electrolyte is composed of 50% carbonates and 50% filler material. The best filler material is β-Alumina ($\beta - NaAlO_2$) which has high electrolytic and ionic conductivity $\Rightarrow$ so, the overall resistance for the cell decreases.

* The electrolyte on the previous form is in the form of sludge $\Rightarrow$ so, liquid amount isn't high $\Rightarrow$ so corrosion problems decrease.
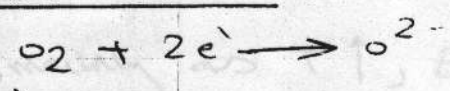
⑤ SOFC

* Can operate till $1000\,°C$.
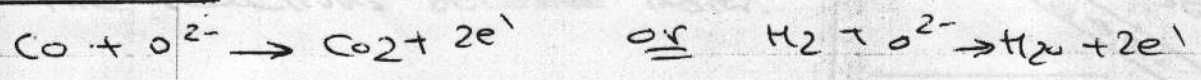* stabilized zirconia is the only used solid oxide.
* H_2, CO or CH_4 can be used as fuel in this case
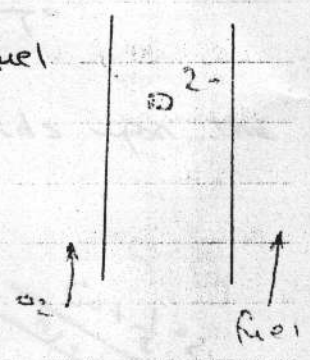* charge carrier : O^{2-}
* **cathode rxn.**

$$O_2 + 2e^- \longrightarrow O^{2-}$$

* **Anode rxn**

$$CO + O^{2-} \longrightarrow CO_2 + 2e^- \quad \underline{or} \quad H_2 + O^{2-} \longrightarrow H_2O + 2e^-$$

* Advantages of this type :-
   1) low corrosion problems
   2) low overpotential because of the highly rate of reactions.

---

* E_0 : Maximum obtainable energy from the cell (voltage at zero current). " $E^\circ = \dfrac{-\Delta G}{nF}$.
* E_0 is used when reactants and products are in their standard states.
   (metals as metals, gases at $1\,atm$).
* If we're not operating at standard states, we'll use Nernest equation

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a\ products\ (activity)}{a\ reactants}$$

$$\alpha = \gamma \ \frac{conc.}{conc.\ at\ its\ standard\ state}$$

activity coeff.

(margin notes:)
$E = E^\circ - \frac{RT}{nF} \ln \frac{p}{...}$
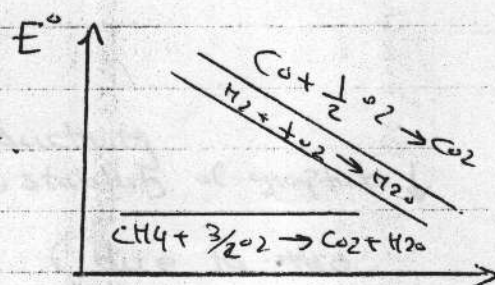activity
$\alpha = \frac{conc.}{conc. at its}$
act. coeff.

$$* \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad, \quad \Delta G = \Delta H - T\Delta S$$

$$\Delta H = \Delta H^\circ + \int_{T^\circ}^{T} \Delta c_p \, dT \quad, \quad \Delta S = \Delta S^\circ + \int_{T^\circ}^{T} \frac{\Delta c_p}{T} \, dT$$

∴ The effect of temp. on E° depends upon the type of rxn as follows.

* So, mainly as $T \uparrow$, $E^\circ \downarrow \Rightarrow$ but also the reactions become faster.

* <u>fuel cell Stack</u>

- Group of fuel cells connected to each other (mainly in series) to get the required voltage.

- Bipolar plates is responsible for the electricity transport between 2 adjacent cells (without high IR drop). So, they must have high electric conductivi[ty]
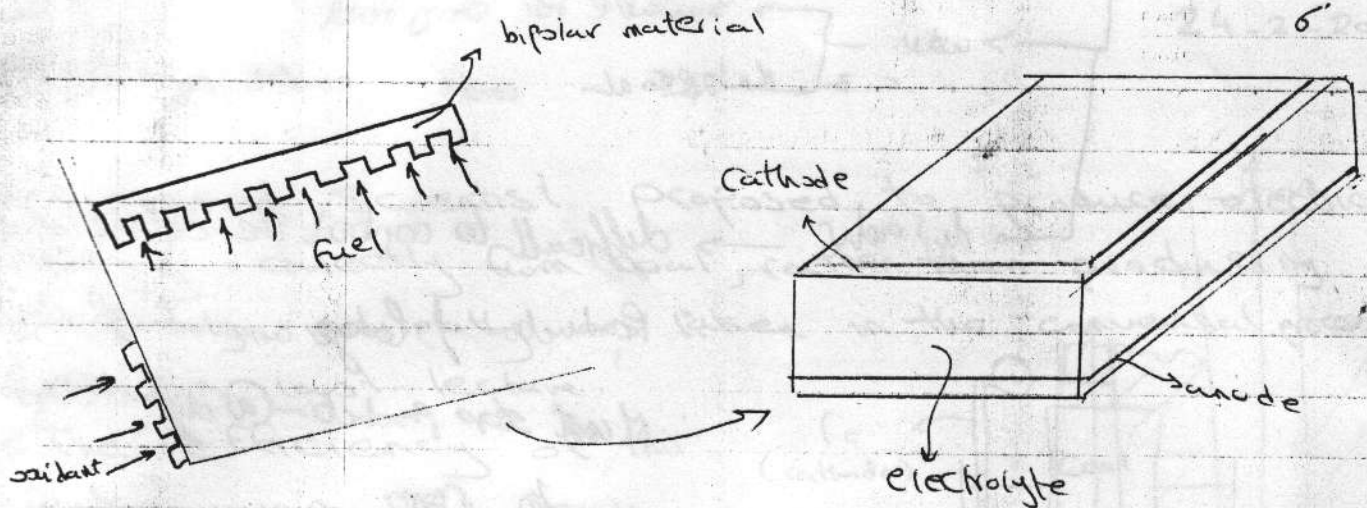
- Bipolar plates must be impermeable to gases

- Graphite is the most usable bipolar plate material.

- Good design for anode and cathode departments must be performed so that high velocity of gases is guaranteed. The high velocity of gases causes high mass transfer $\Rightarrow$ high rate of reactions

$$V = \frac{\textcircled{Q}}{A}$$

So as $A \downarrow$, $V \uparrow \Rightarrow$ so certain design of ducts must be performed as shown $\Rightarrow$

bipolar material

cathode

fuel

oxidant

anode

electrolyte

* <u>Graphite has drawbacks:-</u>
   a) relatively high density
   b) not very high electric conductivity.
   c) expensive   d) as temp ↑, stability of graphite ↓

   - Graphite is banned nowadays (due to their
     use in nuclear reactors).

* Aluminium was suggested to be used as
   bipolar plates, but they face the problem of
   (especially to HF+H₂SO₄) subjection to corrosion. So, coating by
   other (corrosion-resistant) material is needed.

* Titanium can be a 3ʳᵈ alternative, but
   it's more expensive than Aluminium.

lecture 4

Electrolyte matrix (alkaline cells)

* The humidity in the cell should be well controlled to avoid cell drying which would result in contact bet. O_2, H_2 forming explosive mix.

* If the air is dry $\Rightarrow$ H_2O will move from matrix to air by mass transfer $\Rightarrow$ so matrix loses its H_2O content $\Rightarrow$ so, H_2 will contact with air containing O_2 forming explosive mix, so air must be humidified. This won't be problem at 3°C
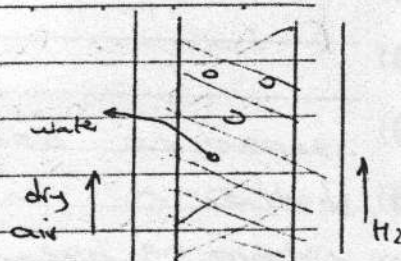
- Introducing air (containing some CO_2) into an alkaline fuel cell is dangerous $\Rightarrow$ this's because by the passage of time, CO_2 will be absorbed into the electrolyte causing the formation of carbonates.

In this ~~case~~ case $\Rightarrow$ CO_2 must be eliminated from the air.

Note

- An idea for energy conservation is (aluminium-air) battery $\Rightarrow$ where $Al(OH)_3$ is formed. Then at certain stations, $Al(OH)_3$ is taken, crystallized $\Rightarrow$ then transferred to Aluminium plants to produce Al $\Rightarrow$ (so, recycling take place)

$$Al + O_2 + H_2O \longrightarrow Al(OH)_3$$
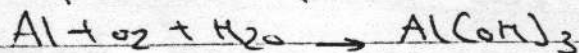
* This method gives high energy density
* The choice of cathode is difficult (as the oxidation takes place in low rates unless we use effective electrodes). Some elements of lanthanides are suggested to be effectively used as electrodes
* The licencers don't state the type of the cathode
* The electrode is sold in $/dcm^2

Electrodes ~~electrocatalyst~~

* After we've studied electrolytes and dipolar metals $\Rightarrow$ we'll study electrodes as the last component in fuel cells.

(i) Electrocatalysts

① Alkaline fuel cells

- Ni, noble metals can be used as anode
- Ni, Nio, silver ∧ ∧ ∧ ∧ cathode
- Asbestos or substitutes can be used as matrix
  (ex: ceramics)

② SPE

- platinum, palladium (noble metals) generally or alloys
  (form thin layer with electrolyte)   can be used as anode
- Noble metals can be used as cathode.
- we don't need matrix

③ PAFc

- platinum can be used as anode
- ∧ ∧ ∧ ∧ ∧ ∧ cathode
- Silicon carbide can be used as
  matrix material. we can't use asbestos as they
 will dissolve in acidic medium.

④ MCFc

- Ni can be used as anode (we
  don't need noble metals as ~~we already~~ are
  already operating at high temp.)
- Ag or lithiated Nio can be used as
  cathode.
- (Al_2O_3 or MgO), $NaAlO_2$, LiO_2 can be used
  as matrix materials.

⑤ SOFc

Compound having bond bet metal and ceramic Cpd →

- ($Co-ZrO_2$) can be used as anode. ($Ni-ZrO_2$)
  cermet can also be used.   (lanthanum oxide + manganese oxide)
- Strontium (Sr) doped → $LaMnO_3$ (lanthanum
  manganate) can be used as cathode.

- The electrode surface must be porous, so that
  the gas transfes to the electrolyte.

electrolyte + matrix

poro

gas

thin film in order not to block the pore
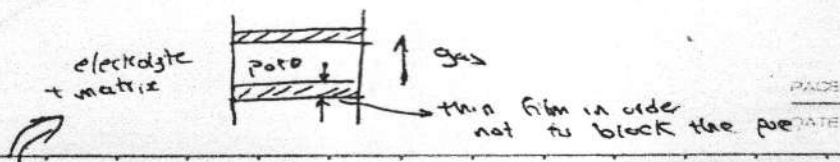
- The electrolyte must perform wetting to certain part of the electrode ⇒ So, thin film is formed.

- The electrolyte mustn't fill the ~~whole~~ pores completely. This'll cause that the distance that the reactant (gas) will take to reach electrode surface will be larger. This phenomena is called flooding. Consequently, overpotential will be high.

- To prevent the occurence of flooding ⇒ the electrode material must contain non-wetting agent. So the electrode composition is :-

(i) carbon black   (ii) certain amount of electro-catalyst inside the carbon block.

(iii) hydrophobic material (pTFE)

- Carbon black is used to load the electro-catalyst. we can't use the electro-catalyst in large amount for economic reasons.

Carbon black

Teflon

electrocatalyst
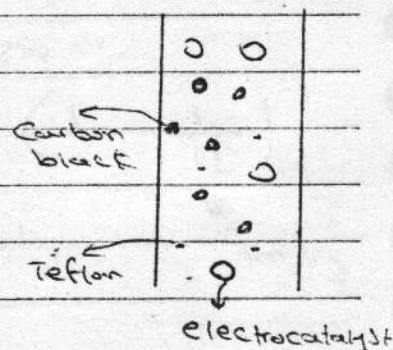
* carbon black must be porous and has high electric-conductivity.

* Carbon black is considered as a support

- Teflon helps to enhance the establishment of the 3-phase interface.

* as the ideal performance is the formation of thin film of electrolyte. So, we've to fix a balance between the pressure difference force (bet gas and electrolyte) and the surface tension of the liquid.

* when Teflon is added in optimum amount, balance bet. the previously mentioned 2 forces will take place ⇒ so, no flooding will take place.

- electrocatalyst enhances the rate of electrode reactions.

---

* The overpotential is mainly a result of 2 components:
   i) activation overpotential ii) concentration overpotential

* $V = E - |\eta|_{cathode} - |\eta|_{anode} - IR_{drop}$

where:-   overpotential

$\eta = \eta_{activation} + \eta_{concentration}$

Tefel eqn (for > 250 mv)

$$= \frac{RT}{\alpha n f} \ln \frac{i}{i_o} + \frac{RT}{n f} \ln \left(1 - \frac{i}{i_L}\right)$$

≈ 0.5

transfer coefficient $(0 \rightarrow 1)$

no. of electrons in electrode reactions

exchange current density

limiting

mainly in liq. phase

$i_L = \frac{nFDC}{\delta}$ → solubility of gas in liquid

depends on mass transfe.

thickness of thin film

$\delta \updownarrow \overline{////////}$

i_o : represents reaction velocity
(so, we use electrocatalyst to increase i_o ⇒ decrease $\eta_{activation}$)

$K = \frac{D}{\delta}$

i_L : by decreasing δ ⇒ $\eta_{conc.}$ decreases